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ENVIRONMENTAL ASSESSMENT ARCSL-EA-83004

**PROGRAMMATIC LIFE CYCLE ENVIRONMENTAL ASSESSMENT
FOR SMOKE/OBSCURANTS**

VOLUME 2 OF 5 VOLUMES

RED, WHITE, AND PLASTICIZED WHITE PHOSPHORUS

PREPARED BY

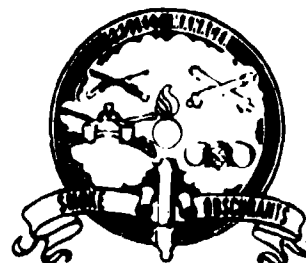
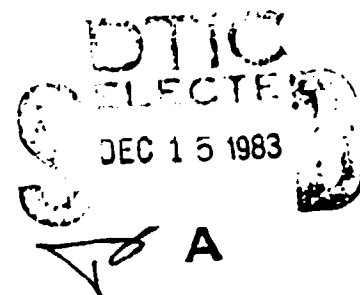
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JULY 1983



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US Army Armament, Munitions and Chemical Command
Chemical Research and Development Center
Aberdeen Proving Ground, MD 21010


Programmatic Life Cycle Environmental Assessment
for
Smoke/Obscurants

Volume No. 2 of 5 Volumes


Red, White, and Plasticized White Phosphorus

July 1983

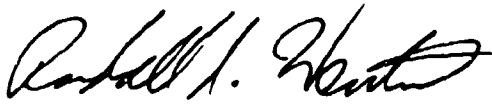
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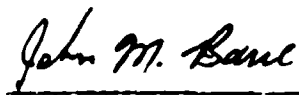
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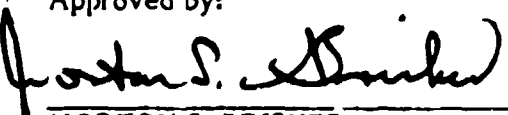
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PREFACE

This is the second volume of a 5-volume series of documents published to provide a general Environmental Assessment (EA) of the smoke/obscuration program. This volume provides pertinent information on red, white, and plasticized white phosphorus. Volume 2 phosphorus smokes; Volume 3, IR smokes; Volume 4, HC smokes; and Volume 5, dye/colored smokes. Volume 2-5 will be published in sequence.

This document is not site or item-specific, however, it is intended for use as a basic document in the preparation of life cycle environmental documentation, as well as a major supportive reference to environmental documentation prepared for individual site-specific operations. Henceforth, as new studies are completed and/or other smoke/obscurants, munitions, are proposed, supplemental information will be published.

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I. PURPOSE AND NEED FOR THE PROPOSED ACTION

As a result of lessons learned from the 1973 Yom Kippur War, both the US Army Training and Doctrine Command (TRADOC) and the US Army Materiel Development and Readiness Command (DARCOM) are placing considerable emphasis on the use of smokes and aerosols as screens and obscurants in combat operations. That war revealed an urgent need for the development of rapid visual screening techniques. Aerosols which block a visual portion of the spectrum, such as white phosphorus (WP) and red phosphorus (RP) smokes, are important items which we must have to screen and obscure our operations from the enemy.

II. DESCRIPTION OF ACTION

A. History.

White phosphorus has been used as a smoke-producing material in munitions since World War I. WP reacts spontaneously with air when released from munitions. As long as oxygen is in contact with WP, the reaction will go to completion. WP forms a dense cloud of white smoke consisting primarily of phosphorus oxides (P_2O_5 , P_4O_6 , P_4O_{10} , etc.), and these oxides react with water vapor to form various phosphoric acids. Despite the excellence of WP as a smoke-producing material, extensive field use during the past revealed a serious inadequacy. Upon dissemination, the resultant smoke cloud forms a pillar and rises, rather than lingering near the surface. When munitions containing WP are functioned, the phosphorus breaks up into minute particles which are dispersed over a large area. Subsequent rapid oxidation of the small particles generates a large quantity of heat which directs the smoke upward. Different approaches were made to correct this fault. In 1944 the problem was solved by plasticizing the WP to reduce the extent of particle shattering when the munitions were detonated. Small granules of WP were added to a viscous solution of synthetic rubber in a solvent which coated the WP with rubber and separated the granules. The newly developed material was called plasticized white phosphorus (PWP). Another development in WP smoke was the WP felt munition. A WP felt munition consists of a felt wedge that is impregnated with WP. Upon deployment, a central burster charge separates the wedges.

Red phosphorus is also used by the military for smoke munitions. It is a reddish solid that can be a finely powdered or a massively formed material. RP is much less reactive with air than WP and is also very insoluble in water.

B. Mode of Dissemination.

There are five basic systems for disseminating phosphorus smoke: artillery, tank guns, mortars, grenades, and aerial smoke systems.

Artillery units can provide smoke support by firing WP-filled munitions. Artillery smoke munitions are available for 105-mm and 155-mm howitzers. These weapon systems can provide obscuration in hard to reach areas.

Tank guns have munitions available for producing smoke for spotting and marking targets, signaling, or dispensing obscuring smoke on small areas. WP-filled munitions are available for 75-mm, 90-mm, and 105-mm tank guns.

The 60-mm, 81-mm, and 4.2-inch mortars can deliver WP-filled munitions for high-volume smoke operations at midranges.

Smoke grenades are used for signaling and for screening small areas. They are used by the individual soldier, who can throw them about 30 to 35 meters. Grenades are also launched by rifles and grenade launchers installed on tanks.

Aerial smoke munitions consist of bombs, bomblets, and rockets. Some rockets, for example, are used in helicopter air delivery systems to produce smoke screens and to mark targets. (Experimental spherical bomblets, disseminated from aircraft mounted dispensers are used in producing aerial smoke.) However, this model was not type-classified.

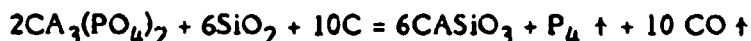
C. Types of Phosphorus Smokes and Smoke Munitions.

White phosphorus, (α- and β-) red phosphorus, (α- and β-) and black phosphorus are considered to be the major modifications of elemental phosphorus. White phosphorus and red phosphorus have military value; black phosphorus does not and will receive no further consideration here. Both red and white phosphorus can be plasticized with a styrene rubber for use in munitions. In this document, WP or P₄ refers to white phosphorus. Elemental phosphorus refers to white and red phosphorus.

1. Chemistry of White Phosphorus.

Two varieties of WP have been identified: α-white, the high temperature form, and β-white phosphorus.¹ β-White phosphorus is the common form of the element produced commercially and that which is used in WP munitions.

WP is prepared commercially by roasting phosphate ores with silica (SiO₂) and coke in an electric furnace.² The silica reacts with the ore to form phosphorus pentoxide which is then reduced to P₄ by the coke. An overall approximation of the reaction is shown by the following equation:



Arrows (↑) indicate that phosphorus (P₄) and carbon monoxide (CO) are emitted as gases or vapors. The P₄ vapor (freed of dust) is cooled and condensed under water to obtain high purity (99.9%) solid WP. WP prepared by this procedure contains arsenic (usually less than 0.02%) and trace amounts of oils (hydrocarbons) as major contaminants.³ Arsenic and other nonhydrocarbon impurities found in a representative sample of WP are shown in table 1.⁴

Commercially prepared WP is a yellowish, waxy solid that is similar to paraffin in appearance and texture. Solid, liquid, and vapor states all contain similar tetrahedral P₄ molecules.⁵ WP melts to a straw-colored liquid, which may have a reddish tinge due to the presence of a small amount of red phosphorus in colloidal form. However, extremely pure WP has either a colorless or white appearance depending on crystal size in the mass. The solubility of WP in selected solvents and other characteristics are summarized in table 2.^{1,2,3,6,8}

Condensed phosphorus vapor and melted red and white phosphorus yield liquids that are similar and that produce WP upon cooling and solidification. Liquid phosphorus is very susceptible to super cooling, and finely divided droplets (1.0 mm or less in diameter) have remained liquid to -71.3°C (115.4 degrees below the freezing point).

Table 1. Representative Concentrations of Inorganic Contaminants in α -White Phosphorus.

<u>Metal</u>	<u>Quantity ($\mu\text{g/gm}$)</u>
Boron	715
Cadmium	0.88
Magnesium	3.6
Zinc	.88
Silicon	377
Copper	1.22
Nickel	0.96
Manganese	0.58
Calcium	18.3
Molybdenum	0.09
Cobalt	0.57
Aluminum	20.0
Vanadium	4.2
Chromium	0.49
Iron	94
Lead	1.28
Barium	0.45
Sodium	9.5
Arsenic	84

Table 2. Characteristics of α -White Phosphorus

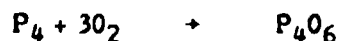
Parameter	Characteristics
Appearance	Colorless, white, or yellow waxy solid
Atomic number	15
Atomic symbol	P
Atomic weight (chemical)	30.975 (ref 8)
Autolignition temperature	30°C (moist air); higher in dry air
Boiling point	280.5°C
Conductivity	Nonconducting
Critical pressure	82.2 atmospheres
Critical temperature	695°C
Crystal structure	Cubic (56 molecules of P_4 per unit cell)
Density	1.828 gm/cm ³
Heat capacity	22.18 cal/mole/degree (25°C); 22.73 cal/mole/degree (44.1°C)
Heat of combustion	710.2 \pm 1.0 kcal/mole P_4
Heat of fusion	600 \pm 3 cal/mole P_4 at 317.26°K
Heat of sublimation	13.4 kcal/mole P_4
Index of refraction	1.8244 (D line, 29.2°C)
Melting point	44.1°C
Molecular formula	P_4
Molecular weight	123.90
Solubility*	
Absolute alcohol	2.5 gm/l
Benzene	28.6 gm/l
Carbon disulfide	1250 gm/l
Chloroform	25 gm/l
Ether	9.8 gm/l
Hot water	Slightly soluble
Water	0.003 gm/l
Almond oil	10 gm/l
Mineral oil	1.45% (room temperature)
Oil of turpentine	16.7 gm/l
Olive oil	12.5 gm/l
Solubility in α -white phosphorus	
Water	3.6 mg H_2O /g P_4 (25 - 45°C)
Mercury	0.29 mg Hg/g P_4 (25°C)
Sublimation pressure	0.025 mm (20°C); 0.122 mm (40°C)
Vapor pressure	1 mm Hg at 76.6°C

*Soluble at 25°C unless otherwise indicated.

WP is chemiluminescent. When it is exposed to compressed air or oxygen at subatmospheric pressure, it undergoes cool oxidation and emits a green glow. This glow phenomenon is responsible for the element being named phosphorus.

If WP is cooled to -76.9°C at 1 atmosphere of pressure, it undergoes transition from the cubic form (density: 1.828 gm/cm^3) to the more dense β -white phosphorus form which crystallizes in a hexagonal system (density: 1.88 gm/cm^3). This shrinkage could produce voids in filled munitions subjected to the above cooling.

α -White phosphorus is by far the most reactive form of elemental phosphorus. The reaction between P_4 and oxygen (oxidation) to produce phosphorus oxides is WP's most important reaction. The reaction occurs spontaneously in air and will oxidize to completion as long as P_4 is exposed to oxygen. Six oxides of phosphorus (P_4O , P_2O , P_2O_3 , P_2O_4 , P_2O_5 , and P_2O_6) have been postulated in the literature; however, only phosphoric oxide, P_4O_{10} (written P_2O_5) and phosphorus trioxide, P_4O_6 (written P_2O_3) have well defined properties. The principal product obtained by burning phosphorus in excess air or oxygen is phosphoric oxide, P_4O_{10} (commonly called phosphorus pentoxide, P_2O_5). This reaction is responsible for the dense white cloud produced when WP munitions are functioned. Combustion of WP in a confined space can produce an oxygen-deficient atmosphere incapable of supporting life. Incomplete combustion due to lack of oxygen may produce lower oxides, especially phosphorus trioxide. Both P_4O_{10} and P_4O_6 are physiologically and chemically hazardous.



Both of these acid anhydrides react readily with atmospheric moisture to produce orthophosphoric acid and phosphorus acid, respectively. The P_4O_{10} molecule is one of the most powerful dehydrating agents known. It will even remove water from materials such as nitric and sulfuric acids and from certain organic molecules.



WP reacts with carbon dioxide at elevated temperatures to produce phosphorus pentoxide and carbon monoxide; therefore CO_2 probably should not be used to fight WP fires.



WP is considered to be a dangerous explosion hazard because of its chemical reactivity with these chemical classes: alkaline hydroxides, halogens, chlorates, iodates, nitrates, and others.

Therefore, these materials would not be compatible for storage with WP. A reaction between WP and one of the above materials also may generate highly reactive and toxic products. For example, the reaction with a concentrated alkali such as potassium hydroxide (KOH) produces phosphine (PH₃) a highly toxic gas, and hydrogen gas (H₂), which is highly explosive.^{1,5}



Oxidizing agents such as chlorine and sulfur also react with WP. In addition, WP combines directly with many or most metals to form metal phosphides, and more than 200 have been identified.⁵ Some of these phosphides react with water on contact to produce phosphine and/or diphosphine (P₂H₄), which are spontaneously flammable. These reactions could be significant for stored WP-filled munitions.

At ordinary temperatures and pressures, WP is practically insoluble and nonreactive with water, and it is safely stored and transported under water. However, at elevated temperatures and pressures, WP reacts with water (steam) to produce phosphine, phosphorus acid, phosphorus pentoxide, and hydrogen.⁵

If WP bricks stored under water undergo prolonged exposure to ultraviolet radiation (sunlight), some of the WP is converted to nodules of amorphous red phosphorus on the surface. Heating WP in a closed system also converts it to amorphous red phosphorus.

2. Chemistry of Red Phosphorus.

Red phosphorus is prepared commercially by heating WP at 350° - 400°C in a closed vessel for several hours. The structure of RP varies from an amorphous to a crystalline solid depending on the method of preparation and subsequent treatment. Its properties vary according to changes in structure; both vapor pressure and thermodynamic effects changed significantly when samples of RP prepared at different temperatures were compared. Commercial RP is primarily an amorphous solid; it is converted to a different crystalline structure upon heating. Interrelationships among known and suspected allotropic modifications of RP are based on the tabulation by Van Wazer (table 3).²

Commercial RP varies in color from pale yellowish-red to dark violet-red⁵ depending primarily on crystal size. The most finely divided crystals tend to appear scarlet-red, while large crystals appear purple when viewed en masse. Surface impurities also affect appearance.

The conversion of liquid WP to RP is "catalyzed" in the initial stages by the addition of iodine (0.01% to 0.1%) or sulfur (0.5% to 1.5%). Molecular structure suggested for amorphous RP includes orderly polymeric chains and random networks of P atoms.

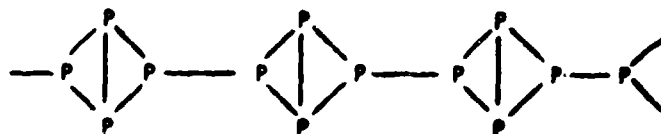


Table 3. Crystalline Variations of Red Phosphorus

Variation	Crystalline structure	Heat of sublimation	Preparation
		kcal/mole	
Red 1	Amorphous	19.7	Commercial product
Red 2	Indefinite (Hexagonal?)	24	Heat 1 to 460°C
Red 3	Indefinite (Hexagonal?)	-	Heat 2 to 520°C
Red 4	Tetragonal	28	Heat 3 to 540°C
Red 5	Triclinic	28.8	Not determined.
Red 6	Indefinite	-	Heat elemental phosphorus at 300°C and 8000 atmospheres pressure.
Brown	Indefinite	Decomposes	Condense hot phosphorus vapor on a liquid-nitrogen cold-finger.

Although RP is not nearly as reactive as WP, it undergoes many similar reactions and yields similar products. Under proper conditions, it will combine directly with halogens, metals, and sulfur; however, it does not react with aqueous alkali.

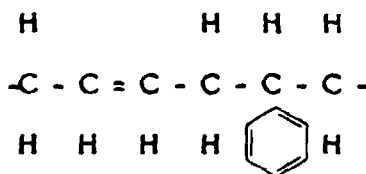
Commercial RP is moderately unstable under normal ambient conditions.⁶ It reacts slowly with atmospheric moisture and oxygen to produce phosphine gas and a mixture of acids. The reaction is exothermic, and the rate of reaction increases as temperature increases. Heat from this reaction might cause spontaneous combustion if RP is stored in sufficiently large piles. The presence of small concentrations of copper, bismuth, silver, iron, and nickel accelerate RP oxidation rate considerably; cadmium and tin have a moderate effect while lead and chromium have little effect.² Aluminum and zinc inhibit atmospheric oxidation. Hydrated aluminum oxide prepared in the presence of RP will inhibit RP's atmospheric oxidation. Commercial RP normally contains iron (approximately 250 ppm) and copper (approximately 30 ppm). Purification of RP to remove these oxidation accelerators greatly increases its resistance to spontaneous combustion.

Since RP is less reactive than WP, reaction conditions are usually more severe. For example, a higher temperature may be required, as in the reaction between RP and chlorine. However, RP is still sufficiently reactive so that an explosion may result upon contact with or friction between it and oxidizing agents such as chlorates, permanganates, or peroxides.

The polymeric nature of amorphous RP tends to reduce its solubility in common solvents, decrease its vapor pressure, etc. relative to WP. Properties of RP are summarized in table 4.

3. Chemistry of Plasticized Red and White Phosphorus.

Both red and white phosphorus have been plasticized with a styrene-butadiene rubber (US Military Specification Mil-R-5: 209 (MU) September 11, 1964) for use in munitions. In the plasticization process, finely divided particles of phosphorus are coated with rubber. The rubber is a hydrocarbon of high molecular weight and consists of the following repeating unit:¹⁰



The ring structure in the molecule is a phenyl group (C_6H_5).

The styrene-butadiene rubber itself is a very inert material; however, it is capable of supporting combustion when it is finely divided. It is very slowly degraded in the atmosphere through reaction with ozone or attack by microorganisms. Reaction products include lower molecular weight hydrocarbons and carbon dioxide.⁴

Upon exposure to the atmosphere or upon ignition, the white and red phosphorus contained in these compositions are capable of undergoing the reactions described above and in sections III.A.1. and III.A.2, respectively.

Table 4. Characteristics of Amorphous Red Phosphorus

Appearance	Reddish-brown, amorphous solid
Autoignition temperature	260°C
Boiling point	280.5°C
Critical pressure	43.1 atm
Critical temperature	589.5°C
Density	2.34 g/cm ³
Heat of combustion	703.2 ± 0.5 kcal/mole
Heat of sublimation	19.7 kcal/mole
Melting point	589.5 C at 43.1 atm
Molecular formula	Highly polmeric
Chemiluminescence	None
Solubility in cold water	Very slightly soluble
Sublimation temperature	416°C

Plasticized RP is referred to by some writers³ as butyl rubber/red phosphorus. Similarly, others⁴ refer to it as red phosphorus-butyl rubber (RP-BR). Butyl rubber is actually a copolymer, such as isobutylene(97%) and isoprene (3%)²⁷ or isobutylene and butadiene.¹⁰ The copolymer of butadiene and styrene is known variously as styrene rubber,¹⁰ styrene-butadiene rubber,⁸ GRS rubber,¹¹ Buna-S,¹¹ etc.

Plasticized white phosphorus has not been produced since 1965. Present plans for the production of plasticized red phosphorus specify the use of butyl rubber. This material is environmentally more acceptable than butadiene-styrene rubber, since neither it nor its degradation products would contain the benzene ring structure (phenyl group).

D. Effects of Climatic/Geologic Conditions on Dispersion Clouds.^{12,13}

The effects of weather, particularly wind speed and direction, and terrain conditions must be considered in smoke screening operations. The movement of smoke depends upon the speed and direction of the wind. Wind direction and velocity determine where to deploy munitions for effective smoke operations. Other factors to be considered are temperature, temperature gradient, humidity, precipitation, and cloud cover. Geological conditions also are critically important to the behavior of dispersion clouds. Details are presented in appendix A.

E. Dissemination Models.

1. Modeling Summary.

Computer model HAZRD2¹⁴ has been developed to predict downwind dosage of aerosols resulting from the operation of one or more smoke-dissemination devices. The program output is suitable for addressing questions of environmental impact and hazard to personnel. A data base of US Army smoke/obscurant systems is built into the model with a provision for user override. Basic program outputs include total dosage as a function of downwind distance, dosage contour half-width dimensions, total areas for the dosages of interest, and a graphic display of dosage contours. A sample is shown in appendix B.

2. Munition Modeling.

Dispersion modeling is available for the following phosphorus munitions:

M2	4.2-inch WP/PWP mortar
M328A1	4.2-inch WP/PWP mortar
M110	155-mm howitzer, WP projectile, (MJ11 E2)
M57	81-mm WP mortar, (M57A1)
M375	81-mm WP mortar, (M875AZ1M37)
MK4	5-inch PWP navy rocket
M60	105-mm howitzer, WP projectile, (M6 A2)
M302	60-mm WP mortar
L8A1	RP Grenade, (12)
M313	90-mm WP gun
M416	105-mm WP gun
M308	57-mm WP rocket, (M3 8A1)
M311	75-mm WP rocket, (M311A1)
CBU-88	RP bomb
XM819	81-mm mortar, 28 RP wedges
XM825	155-mm WP/felt wedge projectile
M116M1	155-mm howitzer, HC, (M116B1)
M259	2.75-inch WP wedge rocket

III. REGULATORY ASPECTS

A. Resource Conservation and Recovery Act.

The Resource Conservation and Recovery Act of 1976 (RCRA), Public Law (PL) 94-580, is the statutory basis for federal regulation of solid and hazardous waste. The US Environmental Protection Agency (EPA) has promulgated regulations implementing RCRA (40 CFR 260-264; 265-267) that identify and provide management requirements for the disposal of solid and hazardous wastes and promote resource conservation and recovery. The regulations list approximately 400 hazardous chemical wastes and 85 process wastes. If not specifically listed, a waste may be hazardous if it exhibits one of the following characteristics (as defined by the regulation): reactivity, corrosivity, ignitability, or toxicity. State and local regulations may also impose more stringent requirements not present in the federal regulations.

The disposal of WP and RP is regulated as hazardous under RCRA because they are ignitable. However, red phosphorus butyl rubber does not display the

characteristics of a hazardous waste. Phosphorus munitions are not considered hazardous wastes until they are programmed for disposal. The demilitarization of WP and RP smokes will form polyphosphoric acids, other less toxic compounds, or other hazardous wastes.

B. Toxic Substance Control Act.

The Toxic Substance Control Act (TSCA) of 1976 (PL94-469) mainly addresses the commercial manufacture, use, and distribution of chemical substances. The act authorizes EPA to obtain toxicity testing before manufacture and the generation of sufficient data on a chemical to predict any environmental hazards associated with its production or use. A manufacturer must notify EPA 90 days prior to commercial production of a new chemical substance.

The use of smoke munitions by the Army for testing and training should not be effected by the TSCA because present smoke materials were developed before the TSCA became effective and were inventoried on the initial TSCA Inventory list (45 FR 505444, 29 July 80).

C. Federal Regulations Governing Oil and Hazardous Substance Release into the Environment.

The policy and procedures for control of discharges of oil and hazardous substances into the environment are detailed in the Federal Water Pollution Control Act (FWPCA) (PL95-576) and the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) (PL96-510). Section 311 of FWPCA describes requirements for the handling of spills of oil and hazardous substances. A "spill" is defined as the release or discharge of regulated pollutants not covered by permit by pumping, pouring, emitting, emptying, leaking or dumping. "Harmful quantities" of a hazardous substance are defined as any discharge that violates state water quality standards adopted by the state and approved by EPA pursuant to section 303 of FWPCA.

EPA has promulgated regulations under the FWPCA which identify and establish reporting requirements for approximately 270 hazardous substances. Reporting requirements are based on harmful quantities as defined by the regulation.

Each Army installation with the capability for a release of a reportable quantity of oil or hazardous substance to the environment is required pursuant to AR 200-1 to prepare, maintain, and implement a Spill Prevention and Countermeasure Control (SPCC) Plan and an Installation Spill Contingency Plan (ISCP). These plans establish procedures to prevent spills and to ensure prompt reporting, containment, and cleanup of spills. Procedures for spill events are outlined in Army Regulation 200-1, 15 July 1982.

CERCLA also establishes reporting requirements for the release of hazardous substances into the environment, including land, air, and water, when release occurs in amounts equal to or greater than the reportable quantity. "Hazardous substance" as defined by CERCLA includes any substance designated or listed in the FWPCA, section 307 and 311; RCRA, section 3001; CAA, section 112; and TSCA, section 7. The reportable quantity for any hazardous substance is one pound, unless otherwise specified in section 311 of the FWPCA.

Elemental phosphorus compounds (WP, RP) are the most stringently regulated compounds with limits of one pound (table 5).

Table 5. Hazardous Substances Under Clean Water Act (EPA, 1979)⁵³

Compound	Reportable Quantity per 24-hour Period
phosphorus (elemental)	1 lb (.454 kg)
phosphoric acid	5000 lb (2270 kg)

D. Clean Air Act.

The Clean Air Act (CAA), PL88-206 as amended, establishes National Ambient Air Quality Standards (NAAQS) for the control of criteria air pollutants to prevent adverse effects to national air resources and to protect human health and the environment. Among criteria pollutant standards, those most likely to affect the smoke/obscurants program are presented in table 6.

Table 6. Federal Ambient Air Quality Standards for Certain Chemicals
(Code of Federal Regulations 1979)

Chemical	National Standards
Particulate Matter	(A) 75 micrograms per cubic meter annual geometric mean (B) 260 micrograms per cubic meter - maximum 24 hour concentration not to exceed more than once per year
Carbon Monoxide	(A) 10 milligrams per cubic meter (9 ppm) - maximum 8 hour concentration not to exceed more than once per year (B) 40 milligrams per cubic meter (35 ppm) maximum 1 hour concentration not to exceed more than once per year

Under the CAA, the country is divided into 247 air-quality control regions (AQCRs) to provide basic geographical units for air pollution control. States are required to prepare State Implementation Plans (SIPs) to implement and enforce criteria pollutant standards in those regions. State standards are often more stringent than federal standards, and vary from one AQCR to another. AQCR's that have attained the NAAQS for a criteria pollutant are considered to be in "attainment" for that pollutant. AQCR's in violation of NAAQS for a criteria pollutant are considered "non-attainment" for that pollutant. Most standards specify two types of limitations - long-term standards which cannot be exceeded on an annual average and short-term exposures which cannot be exceeded for brief periods (e.g., 3 hours and/or 2 hours). By definition, when smokes/obscurants are used in training and testing, the standards for certain criteria pollutants may be temporarily exceeded in the area of the test or training site. The Army environmental coordinator at the individual test or training site should be consulted for coordinating the smoke exercises with the local regulatory agencies for permits or variances as required.

E. Hazardous Materials Transportation Regulation.

1. Transportation.

The transportation or shipment of WP, RP, and PWP must comply with the following federal regulations:

a. Department of transportation regulations.

The Department of Transportation (DOT) formulates the regulations for safe transportation of hazardous materials, poisonous substances, explosives, and other dangerous articles including phosphorus. These regulations are binding upon all carriers engaged in the transport of the above mentioned materials and are in accordance with the best known practices for assuring safety in transit. These regulations also cover the packing, marking, handling, and loading of the hazardous materials to be transported or shipped. The modes of transportation covered by the regulation are surface, air, and water carriers.

(1) The DOT regulations for surface and air carriers governing the safe transportation of hazardous materials, such as phosphorus, and explosive particles by surface and air modes are in accordance with title CFR 49, parts 171-190, and 297.¹⁷

(2) All commercial water carriers transporting hazardous materials are governed by DOT regulations as specified in CFR 46, parts 146-149.¹⁸

b. Military regulations.

Explosives and other dangerous particles such as phosphorus, shipped or transported by the military services are subject to the applicable regulations of the military service involved. Modes of transportation covered by the regulations are as follows:

(1) Surface carriers.

AR 55-355 regulates the movement of military cargo within the US by commercial vehicles. AR 55-56 regulates the shipment of chemical agents under which WP, PWP, and RP are listed.¹⁹

(2) Air shipments.

Air shipments are regulated by TM 38-250 for safe transport of hazardous articles.²⁰

(3) Water shipments.

AR 55-228 regulates shipment and transport of dangerous and hazardous articles by water in conjunction with the US Coast Guard regulations.¹⁸

c. Other regulations.

In addition to federal laws governing the transportation of explosives and hazardous materials, each state and some municipalities have laws or ordinances regulating the transportation of hazardous articles within their jurisdiction.

White and red phosphorus are listed as hazardous materials by DOT (table 7).

F. Other Acts.

Regulations on endangered species or historic preservation are primarily site specific. The environmental quality coordinator for the installation of interest should be contacted.

DA, DARCOM, and TRADOC prohibit the open burning of WP. DARCOM policy is contained in para 4-4f, DARCOM Supplement 1 to AR 200-1. Any request for exception to this policy should be forwarded to the Commander, DARCOM, ATTN: DRCSG, with appropriate justification.

IV. TOXICITY DATA.

A. Mammalian.

1. White Phosphorus.

The oral ingestion of WP in humans can be lethal at levels of 1 mg/kg of body weight. Amounts as low as 0.2 mg/kg of body weight can cause severe effects.³ Acute phosphorus toxicity has a two stage pattern. The initial stage is gastrointestinal irritation with nausea and vomiting. In the second stage the symptoms take on a more severe form. Death can result from cardiovascular collapse.

Table 7. Department of Transportation Hazardous Materials
(Code of Federal Regulation 49, 172.101)^a

Name	Hazard class	Identification no.	Labels required	Packing Sections of CFR 49	Max (Aircraft) net quantity
Red phosphorus	Flammable solid	UN1338	Flammable solid	173,189	Passenger flight forbidden cargo/11 lb
White phosphorus - dry	Flammable solid	UN1381	Flammable solid and poison	173,190	Passenger flight forbidden Cargo flight forbidden
White phosphorus - in water	Flammable solid	UN1381	Flammable solid and poison	173,190	Passenger flight forbidden cargo/25 lb
				25-lb cargo	

Human inhalation of smoke from burning WP has produced throat irritation at levels between 188-500 mg/m³. Table C-1 summarizes the inhalation data on humans. A threshold limit value of 0.1 mg/in³ has been established for WP. Skin contact can produce a severe burn and destroy underlying tissue.³

No toxicity data for humans are available on RP-BR or PWP.³ However, their toxicities should not be greater than that of WP.

A literature review,³ presented a good summary of the toxicity of WP in mammals. Tables which summarize toxic effects of WP and RP are presented in appendix C. In table C-2 the acute toxicological effects of WP are listed. Oral LD50 values for mice and rats were 4.82 and 3.03 mg/kg respectively. Other sublethal acute effects are also presented. The effects on mammals of chronic exposure to WP are in table C-3. Reductions in weight gain and bone growth were observed in rats. Renal and hepatic tissue degeneration were also noted.

Data on the inhalation toxicity of WP, in mammals is presented in table C-4. At smoke concentrations of 110 mg/m³ for one hour, 4 of 20 mice died within 10 days after exposure.

Toxicity studies specific for the combustion of WP felt are presented in table C-5. Brown *et al.*,²¹ observed no lethal effects from WP felt smoke on rats exposed for 15 minutes a day for 65 days to a concentration of 600 mg/m³.

2. Red Phosphorus.

Data on the inhalation toxicity of RP and RP-BR smokes in mammals is presented in table C-6. Weimer *et al.*,²² observed no cumulative toxic effects in rats exposed to approximately 1300 mg min/m³ for 60 days. Weimer *et al.*,²³ reported LCt50 for rats exposed to 222,715 mg min/m³ of RP-BR. Henry *et al.*,²⁴ reported no lethal effects when rats were given 6810 mg/kg oral doses of red phosphorus. Only 1 death in 10 was observed when rats were given oral doses at 10,000 mg/kg of red phosphorus.

B. Aquatic.

The aquatic toxicity of WP, P₄, has been difficult to quantitate due to the reactivity of the chemical. The water solubility of P₄ is 3.3 mg/l.^{7,10} Lai and Rosenblatt²⁵ determined the half-life of WP in water to be between 3.5 and 6 hours. Their data indicate that the rate is dependent on dissolved oxygen, temperature, and pH. Another study found the half-life of WP in water to be 0.85 hours at 30°C.²⁶ Lai and Rosenblatt²⁵ found that the predominant oxidation products for P₄ in water were H₃PO₂ and H₃PO₃. The most recent and most reliable study on the aquatic toxicity of WP was conducted by Bentley *et al.*,²⁷ who detailed the analytical methods and quality control procedures. For a detailed review, see Burrows *et al.*,²⁸ or Sullivan *et al.*,²⁹ Tables C-7 and C-8 present the acute toxicity of WP in several aquatic organisms from static water and flowing water toxicity tests. The most sensitive species was the bluegill sunfish (*Lepomis macrochirus*), with a 192-hour LC50 of 0.6 µg/L (ppb) in a flow-through test.

Bentley *et al.*,²⁷ also conducted chronic, 241-day tests on fathead minnows (*Pimephales promelas*). They found that the eggs spawned from fish exposed to 0.40 and 0.71 µg/L of WP did not hatch. Based on the effects of WP on hatchability at 0.4 µg/L and applying a safety factor of 0.1, Bentley *et al.*,²⁷ recommended a water quality criterion for WP of 0.04 µg/L to protect freshwater aquatic life.

Zitko et al.,³⁰ evaluated the toxicity of WP in marine organisms. They found that the Atlantic salmon (Salmo salar) was the most sensitive species tested with a static 96-hour LC50 of 2.3 µg/L.

When WP and RP smokes are burned, they form various phosphorus oxides.⁵ While phosphorus oxides have a low toxicity in aquatic organisms,⁵ elevated levels in aquatic systems can cause algal blooms and increase the eutrophication of the systems.

C. Wildlife.

The primary contaminants from phosphorus smokes are oxidized phosphorus compounds.¹³ These reacted compounds have a low toxicity and will be rapidly complexed by cations in the soil.⁵

Coburn et al.,³¹ reported on the acute oral toxicity of WP in black ducks and mallards. A single dose of 3 mg/kg of WP was lethal to all ducks in 6 to 33 hours. The mammalian toxicity data indicated that prolonged exposure of wildlife to levels of WP smoke above approximately 1000 mg/m³ may cause sublethal effects. Animals could receive lethal doses of elemental phosphorus if they ingested unreacted smoke materials.

V. ENVIRONMENTAL IMPACTS

A. Research and Development Phase.

Army R&D is subdivided into two phases: Demonstration/Validation and Full Scale Development. During the demonstration/validation phase, smoke generation tests are generally conducted at installations throughout the US and abroad that are selected specifically for their climate and test site (e.g., suitable location, personnel, remoteness, etc.). Site-specific environmental assessments are maintained that describe the environmental setting, including local flora and fauna, and any other features and uses of these installations, such as testing facilities. Decisions regarding full-scale development depend in large part upon the results of the demonstration/validation testing.

1. Alternatives Considered.

No action

Continuation of current R&D on WP, PWP, WP-felt, RP, and RP-BR

2. Environmental Impacts at Activities and Alternatives.

a. No action.

If the R&D effort for phosphorus munitions was stopped, the Army would have one existing type classified munition. Safer and more effective phosphorus munitions would not be developed.

b. Continuation of current R&D of phosphorus munitions.

The research on phosphorus munitions will involve laboratory and field testing of WP and RP formulations. Impacts on the air, soil systems, aquatic systems, and solid-waste generation must be considered when conducting the tests.

Impacts associated with the use of these formulations in conjunction with the development of hardware are addressed generically in this programmatic environmental assessment. Specific impacts resulting from the development of a particular smoke munition will be addressed in more detail in the Life Cycle Environmental Assessment for that item.

(1) Air.

P_4 will spontaneously oxidize when it is exposed to air. Katz *et al.*,¹⁵ conducted laboratory studies to determine the combustion products of WP-felt wedges. They found the major combustion products to be polyphosphoric acids (H_3PO_4 , $H_4P_2O_7$, etc.) Katz *et al.*, also attempted to determine the amount of unreacted phosphorus (P_4) in the smoke cloud; however, poor experimental design and widely varied results made the data of limited value. In addition, they found that only 40% of the WP in the felt wedge burned during the experiments. They observed an oxidized crust on the pads, but had no data on the amounts of oxidized phosphorus and unreacted WP remaining in the pads.

A summary of the environmental fate of phosphorus munitions and their combustion products are presented in table 8.

(2) Soil systems.

The phosphorus combustion products which are deposited on soils will be rapidly complexed and immobilized by metals such as aluminum, absorbed by soil particles, or absorbed by biota.³² Any toxicity of the metal phosphates will depend on the metal. Other than burning vegetation in a localized area, no data on toxic effects of unreacted P_4 on soil systems are available.

(3) Aquatic systems.

Aquatic toxicity data on WP are presented in section IV.B. Upon release into aquatic systems, soluble P_4 is rapidly oxidized. Lai and Rosenblatt²⁵ found that P_4 had a half-life in water between 3.5 to 6 hours and that P_4 was converted primarily to H_3PO_2 and H_3PO_3 . Phosphorus oxides in water will be organically bound (by greater than 90%). Eventually the phosphorus compounds are concentrated in the sediment and organically bound or complexed with metals such as aluminum or calcium.

Prolonged exposure to elevated phosphorus levels in aquatic systems will cause adverse effects. Phosphoric acids may lower water pH in systems with low water hardness. A pH below 5 can be toxic to aquatic organisms. The elevated level of phosphorus compounds in aquatic systems will cause algal blooms and increased vegetative growth. This occurs because phosphorus is usually the limiting nutrient in aquatic systems. The increased nutrient supply to an aquatic system, or eutrophication of the system, will cause detrimental effects on the fish population. Fish kills can occur over the winter due to low oxygen levels. The fish kills occur because the microorganisms utilize the available oxygen in the system by degrading the increased amount of organic matter.

Table 8. Environmental Fate of Phosphorus Smokes and Their Combustion Products^a

Material	Environmental transformation				Environmental fate
White Phosphorus	$P_4 + 5O_2$ P_4O_{10} $P_4 + 3O_2$ P_4O_6	→ → → →	Combustion Atmos, H ₂ O Combustion Atmos, H ₂ O	→ → → →	P_4O_{10} \downarrow H_3PO_4 P_4O_6 \downarrow H_3PO_3
Red Phosphorus	See above		See above		Aquatic and soil fate is oxidation to phosphate via lower oxides
Methylene chloride CH_2Cl_2	Will react with atmosphere radicals to form phosgene, CO ₂				Photochemical decomposition
Phosphorus pentoxide, P_4O_{10}	Reacts with atmospheric moisture to form polyphosphorus acids				Aquatic and soil deposition to phosphates and lower oxides
Phosphorus trioxide, P_4O_6	$P_4O_6 \rightarrow H_2O \text{ vapor} \rightarrow$			\downarrow H_3PO_3	Forms H_3PO_4 , PH_3 , and phosphates
Orthophosphoric acid, H_3PO_4 $H_4P_2O_7$	$pK_1 -2.15$ $pK_2 -7.1$ $pK_3 -12.4$ phosphate				Aquatic and soil deposition formation of phosphate salts
Phosphine, PH_3	oxidized to form oxy-acids of phosphorus				Oxidized or dissociated

(4) Solid waste.

Unburned elemental phosphorus and oxidized phosphorus will remain on the surface of the metal parts and in the felt wedges after the munition has functioned. This material could be a contact hazard to personnel or wildlife.

3. Adverse Effects and/or Conflicts.

Research and development of phosphorus munitions, when conducted in the field, will have several short term (less than 1 month) environmental effects. When the munitions are burned, vegetation in the test area will also be burned. However, the vegetation should be able to grow back. Wildlife may be irritated by the smoke cloud itself. Also, WP is toxic to aquatic organisms at levels lower than 1 $\mu\text{g/L}$ (ppb). Localized fish kills could occur if fragments containing WP fall into an aquatic system. Testing of munitions containing WP should be conducted to minimize the potential for contamination of a water body. RP is not as reactive as WP and will present much less danger to aquatic organisms.

4. Recommended Mitigation.

Information is need in the following areas:

- a. Identification of combustion products of RP
- b. Measurement of deposition rates of combustion products
- c. Measurement of deposition of P_4 onto soil
- d. Measurement of the amount of unreacted P_4 in felt wedges
- e. Measurement of how long unreacted P_4 remains in the wedges
- f. Measurement of how long P_4 remains in the smoke cloud
- g. Monitoring test areas for soil erosion control, if extensive areas of vegetation are burned

B. Manufacturing/Production Phase.

1. Alternatives Considered.

- a. Current production methods
- b. No action

2. Environmental Impacts of Activities Action.

a. Impacts on environment.

WP is produced by Monsanto Chemical Corp., and RP-BR is currently produced in Great Britain. The phosphorus smoke munitions are formulated and loaded at Pine Bluff Arsenal (PBA). Detailed descriptions of the impacts of PBA on the environment are presented in the Pine Bluff Environmental Assessment Statement,³³ and by Berkowitz et al.,³⁴ and Pearson et al.,³⁵

Flow diagrams illustrating the treatments for air, water, and solid wastes generated from the production of WP and RP-BR munitions at PBA are presented in figures 1 and 2. The waste recovery systems and waste treatments are identified for WP. Wastewater and solid wastes from the production of RP-BR munitions were not identified.

b. No action.

Not producing phosphorus munitions would reduce the release of phosphorus in the area around PBA; however, the needs of the military for such munitions would not be met.

3. Adverse Effects and/or Conflicts.

a. Effects.

The formulation and loading of WP and RP-BR munitions are regulated by National Pollution Discharge Elimination System (NPDES) permits. These permits set limits for the release of compounds in the effluents from PBA. The limits established by the Federal Government are judged to have limited adverse environmental effects. Pearson et al.,³⁵ examined the impact of phosphy water (wastewater streams) on receiving water before the NPDES permits became fully effective. Fish kills and excessive phosphorus levels had been observed in receiving waters.

b. No action.

No action would result in no adverse environmental effects.

4. Recommended Mitigation.

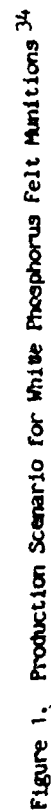
The Army is currently moving toward the increased use of RP munitions. When WP munitions are required, a dry fill process has been developed which is safer for loading personnel and lessens the impact on the environment by greatly reducing the amount of phosphorus-contaminated wastewater.

PBA operations are governed by federal and state air and water quality regulations; therefore, no significant impact should occur from the operation of this facility.

C. Training and Deployment Phase.

1. Alternatives Considered.

- a. Inside testing
- b. Continuation of current training and deployment phase
- c. No action



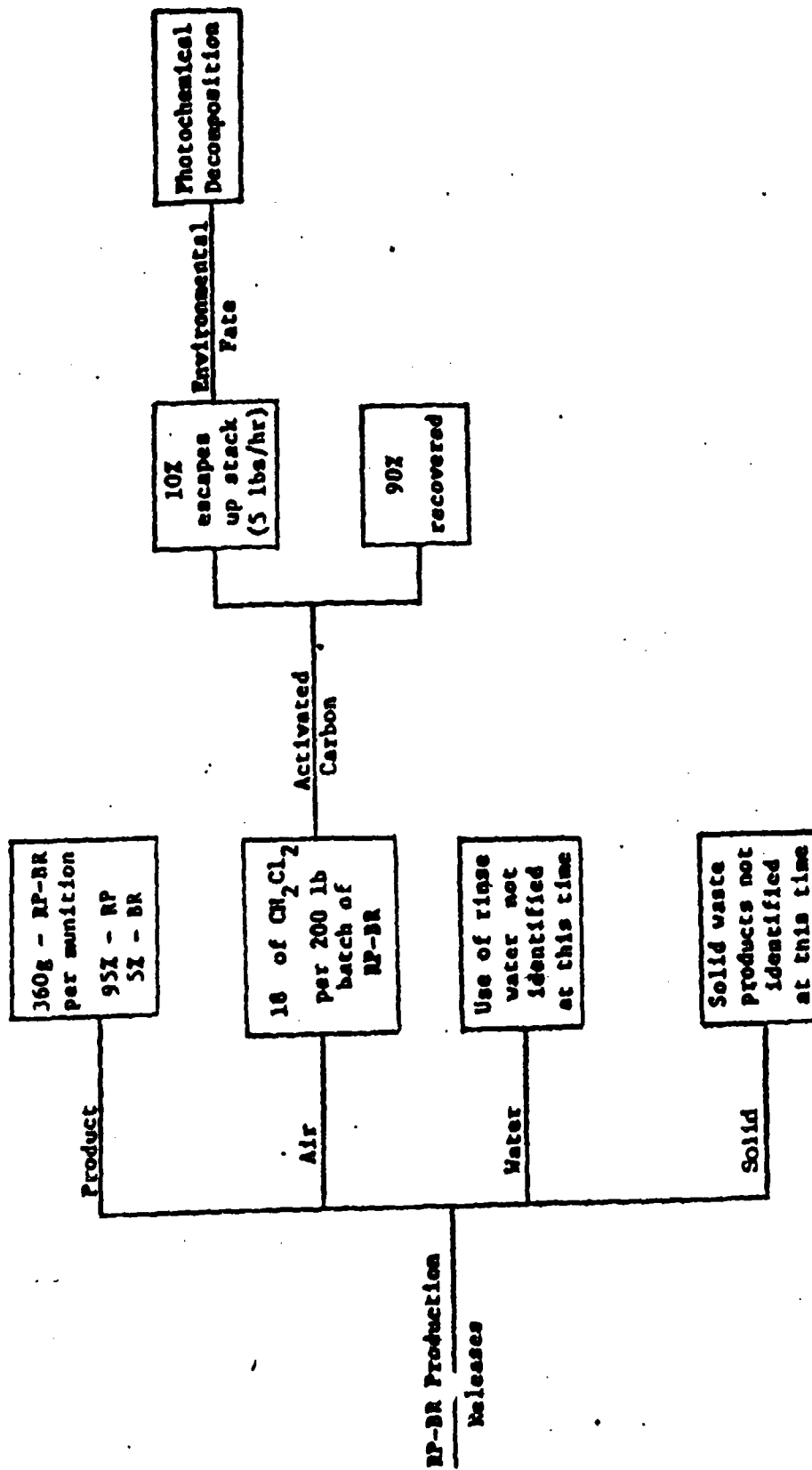


Figure 2. Production Scenario for RP-BR³⁴

2. Environmental Impacts of Activities and Alternatives.

a. Inside testing.

Testing inside would not give personnel a realistic training exercise. However, in projects concerning only equipment operation, inside testing could be considered.

b. Continuation of current training and deployment phase.

The environmental impact of phosphorus munitions during training includes the impacts outlined in section V.A.2.b.

Training and deployment with phosphorus munitions will typically involve a greater amount of material than does research field testing. Environmental impacts for a "worst-case" deployment of WP-Felt smoke during training was calculated by Berkowitz et al.,³⁴ They made the following assumptions:

Training site area = $10,000 \text{ m}^2$ (2.47 acres)*

Frequency of use = 1 hr/week, 52 weeks/yr

Deployment criteria: Maintain obscuring smoke concentrations (0.288 mg/m^3) for 1 hr, neutral stability in a 3 m/s wind.

Deployment frequency: 1 shell/50 sec or 72 shells for the 1-hour training session

Shell fill weight: 5,980 gm of smoke formulation (P_4)

Deployment results in uniform distribution over the training area.

Residual on the ground = 1% of the formulation

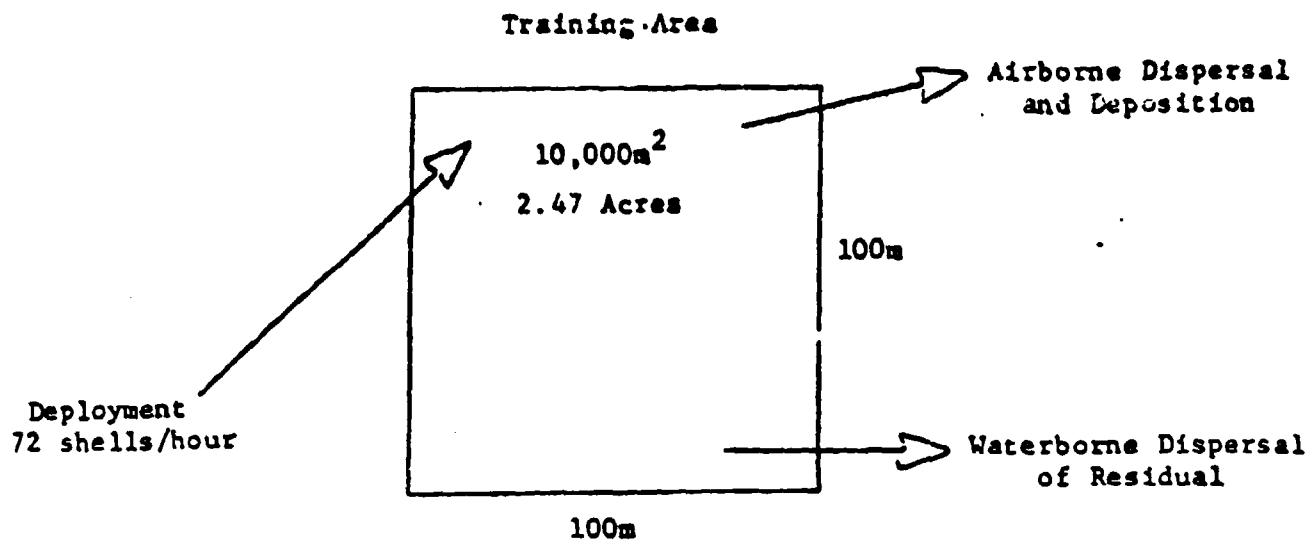
With these assumptions, a residual of 0.43 gm/m^2 of unreacted P_4 is deposited on the surface. When this material oxidizes, some vegetation will be burned; however, other than that the predicted effects on the soil, as described in sec V.A, will be relatively short-term and reversible.

If the P_4 falls into a water body, Berkowitz et al.,³⁴ estimated that water concentrations of 0.43 gm/m^3 or mg/L of P_4 will occur. These levels are 1[^],000 times higher than those estimated as safe for aquatic organisms²⁷ These data emphasize the need for restricting the tests of WP munitions near water bodies.

Concentrations of P_2O_5 in the air were also estimated (table 9). Downwind distances of 5000 m were judged to be safe for humans exposure.

It should be stressed that these calculations were estimated by Berkowitz et al.,³⁴ Little if any field data went into the calculations. The study by Katz et al.,¹⁵ determined that 60% of the phosphorus remained in the felt wedge. The amount of P_4 remaining in the wedge has not been measured.

*See figure 3



5,980g/shell	Smoke formulation fill weight
430,560g/hr	Hourly deployment
4,306g	1% residual
0.43 g/m ²	Uniform Distribution
0.43 g/m ³	Dilution in 1m ³ H ₂ O
22.4 g/m ²	Annual Dose (52 hours)

Figure 3. Training Scenario³⁴

Table 9. Community Exposure Estimates³⁴

Distance downwind from deployment	Maximum concentrations (P_2O_5)	Health effects
	$\mu g/m^3$	
100 m	1.46×10^5	Intolerable concentration = $10^6 \mu g/m^3$ Minimum harassing concentra- tion, masks mandatory = 7×10^5 $\mu g/m^3$
200 m	6.98×10^4	
300 m	4.36×10^4	Lowest toxic concentration = $10^5 \mu g/m^3$
400 m	3.06×10^4	
500 m	2.26×10^4	
600 m	1.84×10^4	
700 m	1.51×10^4	
800 m	1.26×10^4	
900 m	1.10×10^4	
1000 m	9.42×10^3	
5000 m	9.63×10^2	Phosphoric acid TLV = 10^3 $\mu g/m^3$

c. No action.

If testing or training with phosphorus munitions is not performed, the phosphorus load on soils, in the air, and in local water bodies will be reduced. However, military personnel will not be familiar with the uses of phosphorus smoke munitions.

3. Adverse Impacts and/or Conflicts.

a. Inside testing.

If air emissions were controlled, testing inside would not have a significant environmental impact. However, inside training would not be practical for most operations.

b. Continuation of current training and deployment phase.

Training with phosphorus munitions produces several adverse effects. Unreacted elemental phosphorus will initially be present in the area on metal debris from the munition and on the soil surface of the test area. WP is hazardous and will burn personnel or wildlife passing through the area if they come in contact with it. Terrestrial vegetation will be burned, creating areas of bare soil that will result in soil erosion. Runoff from the test area will contain elevated levels of phosphorus oxides that could cause unwanted nutrient enrichment in the receiving water bodies (see sec V.A.2.b). If training is conducted in an area containing a natural water body, fish kills could result from WP contamination.

4. Recommended Mitigation.

The adverse effects from training could be alleviated by the following areas, which are outlined in section V.A.2.b.(4).

Grasses and shrubs that have been burned will recolonize in most areas. However, a desert or arctic environment may require more time for recolonization. Burning of large land areas or larger vegetation should be avoided.

Soil erosion may result if vegetation is burned over a large area. The degree of erosion will depend on terrain, soil type, and weather. Immediate action should be taken to control erosion if it occurs.

D. Transportation and Storage.

1. Transportation.

During the transport of WP or RP, accidental release can occur. RP is relatively stable but will ignite with heat or friction. It will not ignite spontaneously in air. The recommended procedure for RP spill is to cover with an inert filler (sand, clay, etc.) and sweep up. WP is spontaneously flammable upon contact with air; however, and after extinguishing with fog nozzles, re-ignition should be prevented by covering with wet sand or foam. After a fire, the residual elemental phosphorus should be treated as though it contained WP. Any water used on the fire is probably contaminated with WP and should not be allowed to drain into a water body.

2. Storage.

a. Chemical groups.

For purposes of storing and handling, chemical agents are divided into four groups. The definition and description of each group is based on the action of the agent and the degree and type of protection required. Phosphorus munitions are in Group C.

Group C includes materials which are spontaneously combustible (WP and PWP) and for which special fire-fighting techniques and materials are required. Personnel protection must protect against fire and heat. Toxic fumes are a minimal hazard.

At present WP and PWP are the only two chemical fillers in this group. WP filled munitions become liquid at approximately 110°F. This low melting point sometimes causes WP to liquify in stored munitions. If WP-filled munitions are not stored on base in an upright position, when the filler solidifies the center of gravity will shift and produce an erratic trajectory when fired.

b. Quantity distance.

Quantity distance requirements for safe storage of WP munitions are class 1.2 or 1.3 as defined in DARCOM Reg 385-100.³⁶

c. Storage compatibility group.

Munitions filled with WP are listed as Group H in DARCOM Regulation 385-100. Storage incompatibilities are listed in section IC.

d. Impacts of storage.

Spillage and leaking phosphorus munitions in storage are handled in accordance with DARCOM Regulation 385-100 and the Installation's Standing Operating Procedure (SOP).

E. Demilitarization/Disposal Phase.

Demilitarization and disposal operations of WP, PWP, and RP munitions will be in accordance with criteria established in the DOD demilitarization/disposal manual,⁴⁸ and by Demilitarization and Technology Branch, Defense Ammunition Directorate, ARRCOM, Rock Island, Illinois.*

PBA has on-line demilitarization facilities consisting of a download facility, a WP demilitarization facility, an incinerator cluster and support facilities. The incinerator cluster consists of an incinerator with a fluidized bed, a rotary kiln, a chain grate furnace, an afterburner, scrubbers, and related fixtures. The PBA Demilitarization Facilities are designed to handle demilitarization of Army chemicals and disposal of contaminated solid-waste munition parts in an environmentally acceptable manner.* The ash after demilitarization is not classified as a hazardous waste.

*Jakabowski, J. Personnel Communication, 11 February, 1983.

ARRCOM will soon have on-line a relocatable white phosphorus munitions demil plant for the recovery of white phosphorus as phosphoric acid in an environmentally acceptable manner.

VI. AGENCIES/PERSONS CONTACTED

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VII. CONCLUSIONS

The impact of the use of phosphorus munitions on the environment is typically short term and reversible. The reasonable use of phosphorus munitions during research or training should not have any long term effects. The loading of phosphorus munitions at PBA is regulated by various safety and environmental laws and permits. If PBA operates within stated limits, the environmental effects from the loading of phosphorus munitions should be minimal. Phosphorus munitions are hazardous materials are strictly regulated during transportation and disposal. If regulations are followed, the environmental impact of the munitions during these phases of use should not be significant.

The amount of phosphorus released into the environment by the Army is small when compared to its release from detergents and fertilizers. The environmental reactions and products from phosphorus munitions are known (table 8). The phosphates resulting from the munitions will act as nutrients to the receiving systems:

The information generated from this environmental assessment supports a Finding of No Significant Impact (FNSI). A statement of No Significant Impact with mitigation will be published in accordance with Title 40, Code of Federal Regulations, part 1508.13. Information on phosphorus munitions is needed in the following areas:

- a. identification of combustion products of RP
- b. measurement of deposition rates of combustion products
- c. measurement of the deposition of P_4 onto soil
- d. measurement of the amount of unreacted P_4 in felt wedges
- e. measurement of the half-life of unreacted P_4 in the wedges
- f. measurement of the half-life of P_4 in the smoke cloud
- g. monitoring test areas for soil erosion control, if extensive areas of vegetation are burned
- h. toxicology and environmental fate of RP-BR

These data will give the Army a more complete picture of the environmental effects of phosphorus munitions. However, the lack of this information does not mean that there are significant and uncertain environmental effects produced from the use of phosphorus munitions.

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APPENDIX A
EFFECTS OF CLIMATIC/GEOLOGIC CONDITIONS ON DISPERSION CLOUDS

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1. Effects of Weather.

a. Winds.

Prevailing (steering) winds have the greatest influence on smoke operations. These winds exist between 9 and 800 meters above the ground surface. When produced smoke moves to the level of the prevailing winds. The data on prevailing winds are commonly measured at 16 meters.

b. Wind Speed.

The prevailing wind speed determines how far the smoke-producing equipment should be placed from the vital area to be screened/obscured. Wind speeds ranging from 5 to 15 knots per hour are considered best for producing militarily effective smoke. Some types of smoke behave differently in different winds. For example, WP smoke tends to pillar if wind speed is less than 9 knots. Wind speeds in excess of 15 knots per hour carry the smoke rapidly from its source; therefore, more smoke equipment and/or material are required to produce the desired results.

c. Wind Direction.

Wind direction is defined as the direction from which the wind blows. The direction determines the location of the smoke line to cover the vital area. Wind direction is classified as head wind, tail wind, and flank and quartering winds. Head winds blow away from the smoke objective or vital area and directly to the smoke-producing source. Tail winds are the opposite of head winds. Flank winds blow across the smoke objective and smoke source. Quartering winds blow between the other winds. Another system for surface wind designation relates wind direction to cardinal and intermediate points of the compass (north, northeast, east, southeast, south, southwest, west, and northwest).

d. Temperature Gradient.

There are three types of temperature gradients that affect smoke screens: inversion (complete sky coverage), neutral (30% or 70% sky coverage), and lapse (clear to less than 30% sky coverage). An estimate of temperature gradient is used to predict the stability of the air. Temperature gradients are measured by subtracting the air temperature 0.5 meter above the ground surface from the air temperature 4.0 meters above the surface.

(1) Inversion (stable).

A stable condition exists when the air temperature increases with an increase in altitude. This condition creates stable air currents and causes smoke to linger for long periods. Under stable conditions, smoke streamers tend to travel parallel downwind for long distances before they spread and merge into a continuous blanket of smoke. Even after merging, this blanket of smoke lies low to the ground and reduces visibility at ground level. Stable conditions may keep smoke from rising high enough to cover the tops of building or other tall objects.

(2) Neutral.

When there is little change in temperature based on altitude, conditions are neutral. Under neutral conditions, smoke streamers have steadier direction and there is less tendency for them to rise than when conditions are unstable.

Also, streamers tend to spread and rise more quickly than under stable conditions. Therefore, neutral temperature gradients are best for smoke purposes.

(3) Lapse (unstable).

Unstable conditions exist when air temperature decreases with an increase in altitude. Unstable conditions cause smoke breakup because the air is moving. In low winds, the smoke streamer may rise abruptly from the source. In higher winds, the streamer may pass only a short distance downwind before rising and becoming diffused. Therefore, a lapse condition is considered poor for the use of smokes.

e. Humidity.

The WP smoke particles absorb moisture and increase in size, thereby increasing their mass density and making the smoke more effective. Most smoke munitions produce a denser smoke when the humidity is high, therefore, high humidity is always favorable for smoke employment of WP.

f. Precipitation.

Light rains decrease visibility; therefore, less smoke is needed for concealment. Heavy rain and snow so reduce visibility that smoke is rarely necessary to provide concealment.

g. Cloud Cover.

When the sky is more than 70 percent covered with clouds, neutral temperature gradient conditions usually prevail. The atmosphere is moderately stable, and conditions are generally favorable for smoke.

2. Geological Conditions.

a. Terrain.

Since smoke is carried by the wind, it normally follows the earth's contours. On flat or unbroken terrain and over water, smoke streamers take longer to spread out and mix. On the other hand, trees and buildings tend to mix smoke streamers and increase smoke coverage. Large hill masses and rugged terrain cause strong crosscurrents which disperse smoke, causing holes and unevenness.

b. Arctic.

Smoke operations in arctic regions or other cold weather areas present special problems common to all types of units. On clear days, stable conditions exist over snowy surfaces. This condition is strongest about sunrise. Smoke tends to remain near the surface and may travel for long distances before dissipating. Under extremely cold conditions, smoke clouds last longer than under moderate temperatures. Snow and fog so reduce visibility that much less smoke is required for effective screening.

c. Desert.

All deserts have certain characteristics in common - lack of surface water, little vegetation, large areas of sand, extreme temperature ranges, and brilliant sunlight. Because of meteorological conditions and the vast areas usually

available for dispersing and maneuvering troops, it is difficult to make beneficial use of smoke units. However, smoke can be used effectively for screening and deception. Smoke may be employed to screen an installation or the breaching of barriers and minefields and to cover artillery positions at night to reduce muzzle flash. Desert sands absorb heat from the sun and cause appreciable differences in horizontal temperature which in turn may cause whirlwinds. The soil is heated during the day to such an extent that smoke operations become extremely difficult because of strongly unstable conditions. Smoke tends to pillar because of rising air currents. High winds and dust storms occur throughout the year. Smoke is more effective in early morning and late evening or on an overcast day when neutral atmospheric conditions exist.

d. Mountain.

Mountain operations are characterized by the difficulties encountered due to terrain. Generally, inadequate road nets found in mountain areas enhance the military value of existing roads and add importance to high ground that dominates other terrain. Smoke generators can screen artillery positions, supply routes, and preparations for installations and entrenchments. Smoke can also reduce the enemy's ability to use high ground for observation. Small smoke units are often required to operate for extended periods with limited resupply in mountain operations because of transportation difficulties. Steep hills split winds so they eddy around and over the hill. Thermally induced slope winds occur throughout the day and night. These conditions make it extremely difficult to establish and maintain smoke screen. Wind currents, eddies, and turbulence must be continuously studied and observed.

e. Jungle.

The jungle ordinarily affords concealment from air and ground observation. Smoke screens may be employed in jungle operations to screen aircraft landing areas, to help prevent observed fire on helicopters approaching landing zones, and to screen landing zones while troops debark helicopters.

In many instances, smoke use may be limited to coastal regions to conceal landings. In other areas, smoke may be used to conceal river crossings or to provide coverage of rivers used as routes of communication. Smoke used in dense vegetation tends to spread slowly downwind and downslope and follow creek beds and gullies. Jungle weather is usually hot, humid, and characterized by sudden changes. Within only a few minutes, clear, hot weather may change to torrential downpour. Windspeed in jungle areas normally does not exceed 3 kilometers per hour.

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APPENDIX B
SAMPLE SMOKE MODEL

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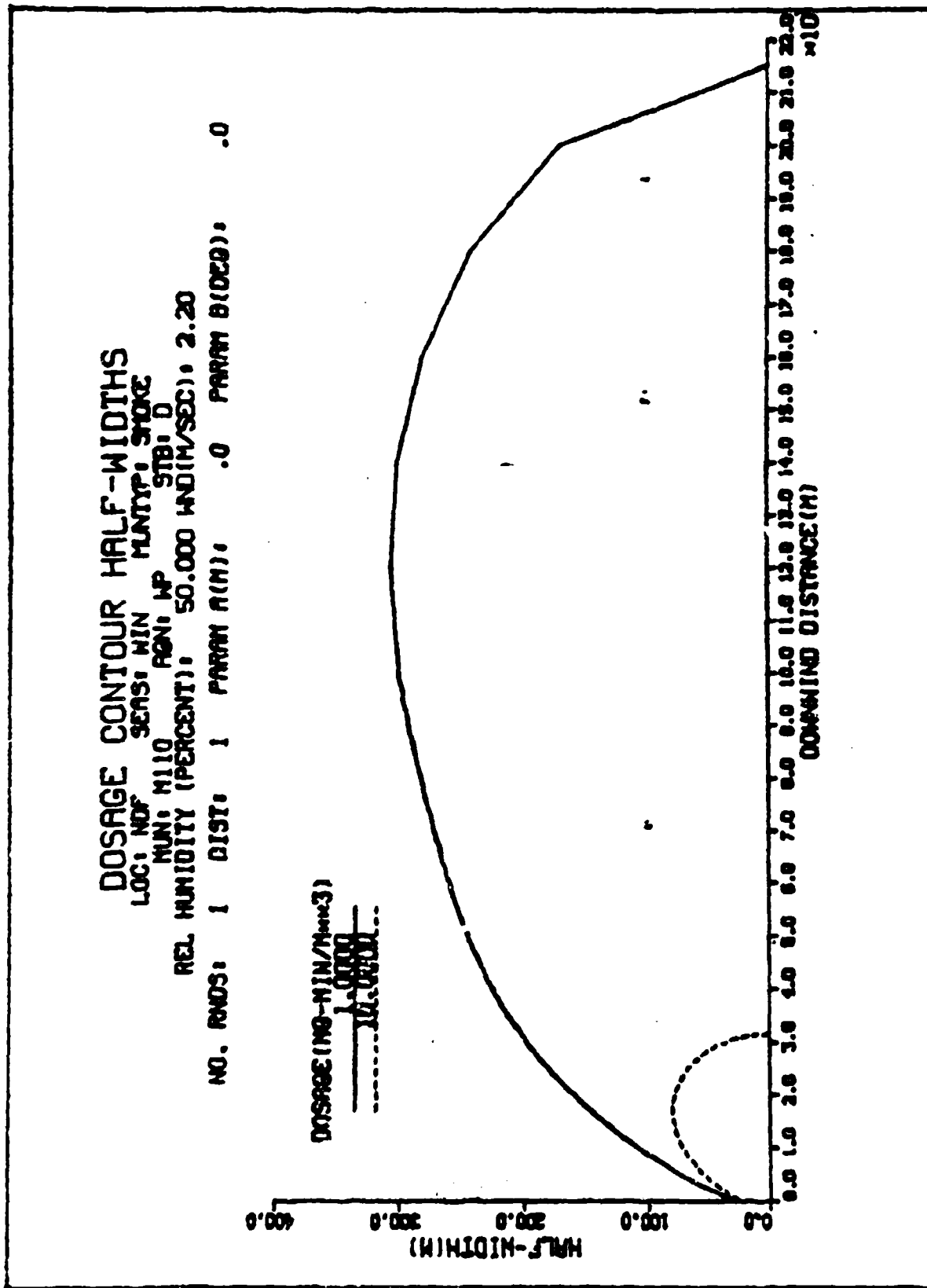


Figure B-1. Dosage Contour Half-Widths

M110 DOWNWIND DISTANCE VS DOSAGE

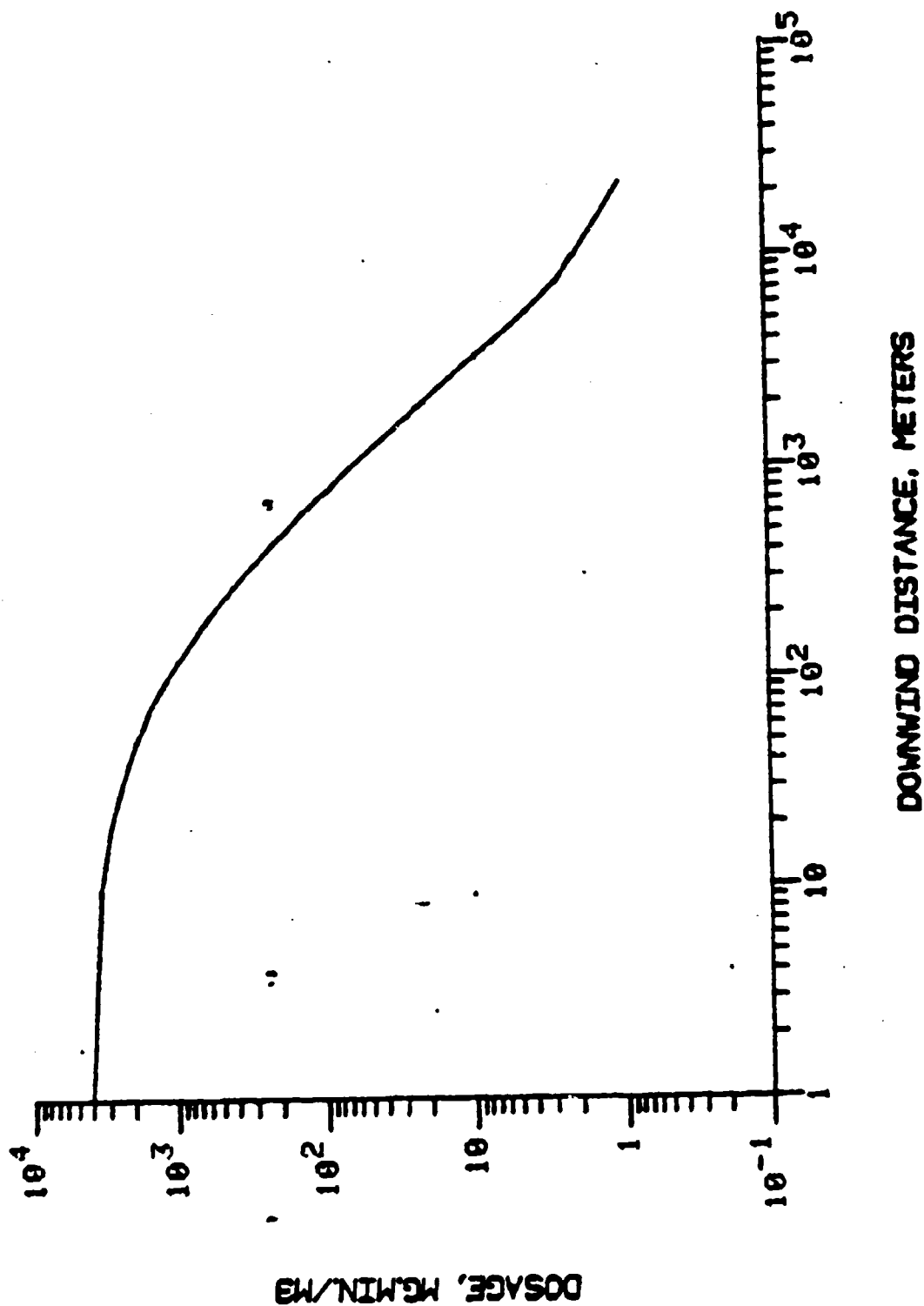


Figure B-2. M/10 Downwind Distance vs. Dosage

APPENDIX C
TOXICOLOGICAL DATA ON WHITE AND RED PHOSPHORUS

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Table C-1. Inhalation Toxicity of Smoke From Burning White Phosphorus in Humans²⁵

Number of subjects	Concentration of white phosphorus smoke	Length of exposure	Effects Observed
	mg/m ³	min	
108	1000	Not specified	Intolerable
108	700	Not specified	Minimum harassing concentration
Not specified	592	3.5	Respiratory distress, nasal discharge, coughing, throat irritation
	588	2	soreness
7	514	16	Nose and throat irritation, coughing during exposure
6	453	10	5/6 subjects showed throat irritation. One experienced nausea and nasal discharge during 3 days after exposure
6	425	15	Nose and throat irritation during exposure but no remarkable effects during 3-day observation period after exposure
5	408	10	4/5 subjects had throat irritation and coughing. One experienced sore throat and symptoms of cold during 3-day observation period after exposure
7	188	5	5/7 experienced throat irritation, coughing, and slight headache during exposure. Twenty four hours later, four subjects had frontal headache, nasal congestion, throat irritation and coughing. After 2 and 3 days only one subject showed signs of respiratory irritation.

Table C-2. Pathologic Observations Made in Acute Toxicity Studies of White Phosphorus in Animals

Species	Dose	Route of Administration	Effects Observed	Reference
Mice	4.32-4.85 mg/kg	oral	LD50, anorexia, jaundiced and enlarged liver	Lee et al. ¹
Rats	3.30-3.07 mg/kg	oral	LD50, anorexia, jaundiced and enlarged liver	Lee et al. ¹
Rats	10 mg/kg	oral	Fatty infiltration and/or degeneration of liver biochemical changes in liver	Paul et al. ¹
Dogs	0.05 mg/kg	oral	Fatty degeneration of liver and hepatic insufficiency	Williamson and Mann ³
Dogs	0.2-0.4 mg/kg	subcutaneous	Gastrointestinal lesions	Buchanan et al. ⁴
Dogs	5 mg/kg	subcutaneous	Fatty degeneration of liver and hepatic insufficiency	Bradenky ⁵
Mice	0.0125% 0.05%	subcutaneous subcutaneous	Morphological deformation of mitochondria	Scott ⁶
Rabbits	1.6-10 mg/kg	subcutaneous	Adrenal insufficiency	Neubauer and Porges ⁷
Rabbits	0.1% in peanut oil	skin application	No skin irritation	Lee et al. ¹
Rats	140 mg/kg	skin application	Burns, changes in blood and urine biochemical chemistry, fatty, degeneration and nephritis in kidneys	Ben-Hur et al. ⁸
Rabbits	3000 mg/kg	skin application	Burns, decrease in serum calcium increase in serum phosphorus	Bowen et al. ⁹
Rabbits	160 mg/m ³	inhalation	Decrease in hemoglobin and erythrocyte counts	Maruo ¹⁰
Mice	500 mg/m ³	inhalation	Death within 10 minutes	NIOSH ¹¹

Table C-3. Chronic White Phosphorus Toxicity in Animals²⁵

Species	Dose and Route of Administration	Duration of Administration	Effects Observed	Reference
Dogs	0.1 mg/kg body weight/day (subcutaneous)	56 days	Hydropic renal degeneration	Buchanan, et al. ⁴
Dogs	0.2-0.8 mg/kg body weight/day (oral)	37 days	Shifts in plasma proteins ¹²	Lang and Frenkel ¹³
Rats	0.0027 mg/kg body weight/day (oral)	25 weeks	Slight reduction in weight gain	Sollman ¹⁴
Rats	0.0032 mg/kg body weight/day (oral)	22 weeks	No ill effects until 15 weeks, then a slight reduction in weight gain.	Sollman ¹⁴
Rats	0.018-0.07 mg/kg body weight/day (oral)	22 weeks	Reduction in weight gain	Sollman ¹⁴
Rats	0.01% in cod liver oil (oral)	22-57	Reduction in weight gain and retardation of longitudinal bone growth.	Adams and Sarnat ¹⁵
Guinea pigs and rabbits	0.6-1 mg/kg body weight/day (oral)	4 months	Liver cirrhosis	Mallory ¹⁶
Guinea pigs	0.75 mg/kg body weight four days/week (oral)	35 weeks	Destruction of hepatic parenchyma	Ashburn et al. ¹⁷
Rabbits	0.3 mg/kg body weight/day oral	117 days	Reduction in weight gain and retardation of longitudinal bone growth	Adams and Sarnat, ¹⁵
Rabbits	0.2-1 ml of 1% solution of phosphorus in oil twice or three per week (intravenous)	15 weeks	Nerve degeneration in central nervous system	Ferraro et al. ¹⁸

Table C-4. Inhalation Toxicity of White Phosphorus Smoke
in Animals After One Hour Exposure²³

Species	Concentration of Smoke	Effects Observed
	mg/m ³	
Mice	110	No deaths during exposure; 4/20 animals died at 24 hr, 48 hr, 5 days, and 10 days post exposure, respectively.
	900	No deaths during exposure. Some animals died 24 hr to 10 days post exposure.
	1230	5/20 animals died during exposure; more deaths 24 hr to 10 days post exposure.
	1510	3/20 animals died during exposure; more deaths 24 hr to 10 days post exposure. Death in all cases was due to respiratory failure. Other effects observed were hemorrhage in the lungs and occasional cloudy swelling of the heart, liver, and kidney cells.
Rats	380-4800	Only 1/10 died during exposure (4530 mg/m ³)
	380-2150	No deaths during exposure; only one death (1/10) at 1350 mg/m ³ during 24-48 hours post exposure.
	4460-4810	5/10 died 1-10 days post exposure. Autopsy findings showed pulmonary congestion, edema, occasional atelectasis and cloudy swelling of the liver and kidney cells.

Table C-5. Toxicity Studies of Mammals of White Phosphorus Felt

<u>Animal</u>	<u>Administered</u>	<u>Dose</u>	<u>Effect</u>	<u>Reference</u>
Rat Sprague-Dawley	inhalation 15 min/day, 5 day/wk 13 weeks	1160 mg/m ³	LC40	Brown et al. ¹⁹
Rat	inhalation 15 min/day; 5 day/wk 13 weeks	600 mg/m ³	no deaths	Brown et al. ¹⁹
Rat	oral	1.48 ml/kg	LD50	Manthel et al. ²⁰
Rabbit	eye irritation	0.1 ml (WP in corn oil)	Severe	Manthel et al. ²⁰
Rabbit	skin irritation	0.5 ml (WP in corn oil)	Severe	Manthel et al. ²⁰
Rat	inhalation	94,100 mg min/m ³	LCt50	Brown et al. ²¹
Guinea pig	inhalation	5300 mg min/m ³	LCt50	Brown et al. ²¹

Table C-6. Inhalation of Red Phosphorus Smokes to Mammals

Animal	Compound	Administered	Dose	Effect	Reference
<i>mg min/m³</i>					
Sprague-Dawley rat	RP	8 min/day; 5 day/wk 12 weeks	1319 ± 269	No irreversible toxic effects (redened eyelids)	Weimer et al. ²²
ICR swiss mice	RP	8 min/day; 5 day/wk 12 weeks	1319 ± 269	Male weight loss	Weimer et al. ²²
Harley guinea pig		8 min/day; 5 day/wk 12 weeks	1319 ± 269	No toxic effects	Weimer et al. ²²
Rat	RP/BR	-	222,715	LC ₅₀	Weimer et al. ²³
Guinea pig	RP/BR	-	4040	LC ₅₀	Weimer et al. ²³

Table C-7. Acute Toxicity Values^a for Elemental Phosphorus Utilizing Aquatic Invertebrates and Fishes Determined During Static Bioassays (nominal concentrations)²⁴

Species	Toxicity values (µg/l)		
	24 hr	48 hr	96 hr
<u>Daphnia magna</u> (water flea)	34 (28-41) ^b	30 (25-37)	-
<u>Gammarus fasciatus</u> (scud)	> 420 < 560	250 (190-310)	-
<u>Asellus militaris</u> (sowbug)	> 420	> 560	-
<u>Chironomus tentans</u> (midge)	260 (210-330)	140 (110-190)	-
<u>Lepomis macrochirus</u> (bluegill)	27 (22-32)	9 (5-16)	6 (4-9)
<u>Salmo gairdneri</u> (rainbow trout)	61 (39-98)	28 (16-48)	22 (15-32)
<u>Ictalurus punctatus</u> (channel catfish)	152 (99-232)	87 (69-109)	73 (53-99)
<u>Pimephales promelas</u> (fathead minnow)	101 (73-141)	34 (24-46)	20 (16-25)

^a Acute toxicity values are expressed as effective concentrations causing immobilization (EC50) after 24 and 48 hours for invertebrates, and lethal concentrations (LC50) after 24, 48, and 96 hours for fishes.

^b Confidence interval of 95 percent

Table C-8. Acute Toxicity of Elemental Phosphorus to Fishes and Aquatic Invertebrates During Dynamic Bioassays.²⁴

Species	LC50 ^a (μg/l)			
	24 hr	48 hr	96 hr	Incipient ^b
<u>Daphnia magna</u> (water flea)	> 50	> 50	-	11 (5-24) ^c
<u>Chironomus tentans</u> (midge)	> 240	111 (31-399)	-	20 (4-99)
<u>Lepomis macrochirus</u> (bluegill)	> 3.2		2.4 (1.7-3.5)	0.6 (0.4-1.1)
<u>Ictalurus punctatus</u> (channel catfish)	> 19		> 19	4.2 (3.3-5.4)

^a LC50 values are based on nominal concentration for water flea, midge, and bluegill and on mean measured concentrations for channel catfish.

^b Incipient LC50 estimated after 192 hours for water flea, 120 hours for midge, 192 hours for bluegill, and 624 hours for catfish.

^c Confidence interval of 95 percent

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